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MERCURY IN CANADIAN NON-FERROUS METALS EXTRACTION CIRCUITS. PART 1 - HUDSON BAY MINING AND SMELTING COMPANY, LIMITED, FLIN FLON, MANITOBA

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MERCURY IN CANADIAN NON-FERROUS METALS EXTRACTION CIRCUITS. PART 1 - HUDSON BAY MINING AND SMELTING COMPANY, LIMITED, FLIN FLON, MANITOBA

by

T.T. Chen* and P. Pint*

1. SUMMARY

Mineralogical and chemical analyses for mercury and its compounds in the feeds to the smelter of Hudson Bay Mining and Smelting Company indicate that mercury is found primarily in solid solution in sphalerite, chalcopyrite, tetrahedrite and tennantite. Mercury cannot be separated from zinc concentrates by minerals beneficiation techniques prior to chemical processing; however, some lowering of mercury concentration of the copper concentrates may be possible. Of the total mercury entering the HBMS processing circuit, 69% is associated with the zinc concentrates and 31% is with the copper concentrates.

During pyrometallurgical processing, virtually all the mercury contained in the copper and zinc concentrates is released to the gas phase, but some of the evolved mercury collects in or on dusts in the gas cleaning systems.

Mercury distribution between dusts and gases depends on the temperature and on the nature of the dusts. The sequence of decreasing mercury concentration in the dusts is, first,

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the unoxidized copper sulphides in the electrostatic precipitator (∿180°C) dust from the copper concentrate roasters, followed by the copper circuit baghouse (140°C) dust wich is composed primarily of ZnO, followed by the coarse-grained Fe_2O_3-$ZnFe_2O_4$-ZnO dust from the zinc circuit ESP (275°C).

The only processing options available for decreasing the amount of evolved mercury appear to be a separate treatment of the dusts from the copper circuit which could isolate about 10% of the total mercury and the lowering of the ESP temperature in the zinc circuit followed by dust treament which could further isolate an additional up to 65% of the mercury.

2. FOREWORD

In an effort to reduce the emissions of potentially hazardous compounds or elements from pyrometallurgical processes, a project was initiated to determine the occurrences of toxic elements in Canadian sulphide ores and concentrates[1], to determine their distribution in processing circuits and to evaluate methods for minimizing emissions of these toxic elements. Mill concentrates and smelter dusts from Hudson Bay Mining and Smelting Co., Ltd. (HBMS), Flin Flon, Manitoba, were studied to identify the principal carriers of mercury and to establish the distribution of this element in the pyrometallurgical circuits. These data indicate the behaviour of mercury during processing and will aid in the selection of abatement technology. This report summarizes findings on mercury deployment at the Flin Flon copper and zinc smelters.

3. HBMS COPPER AND ZINC PROCESSING CIRCUITS

At the Flin Flon plant, copper and zinc concentrates are processed to produce slab zinc, anode copper and cadmium metal. The unit operations employed have been adequately described in the literature[2,3,4]. The flow sheet is shown in Fig. 1. Besides treating its own copper and zinc concentrates (e.g., Flin Flon, Chisel Lake, Snow Lake), the Company also processes custom concentrates from Fox Lake and Ruttan Lake in northern Manitoba, the Pine Point mine in the N.W.T, the Whitehorse, Yukon, orebody and others. When the current sampling compaign was undertaken, concentrates from Snow Lake, Chisel Lake and Flin Flon were combined to produce a blended feed called Hudson Bay concentrate, which was mixed with custom concentrates. The combined zinc concentrate is fed directly to the zinc roasters; flux is added to the combined copper concentrate to form the copper smelter feed. Table 1 summarizes the mercury concentration of the various concentrates as well as their contribution to the total input of mercury to the smelter.

In the zinc circuit shown in Fig. 1, the zinc concentrate (averaging approximately 50% Zn, 11% Fe, 0.8% Cu, 7% H_2O) is roasted and the calcine is subjected to conventional leaching, followed by solution purification, electrolysis and casting to produce slab zinc. The roaster dust collected in the Cottrell electrostatic precipitators is recycled to the roasters. The cleaned gas is emitted to the atmosphere.

In the copper circuit (Fig. 1), the copper concentrates and flux (10 to 15%) are combined with zinc leach residue from

the zinc circuit. The approximate composition of the concentrate is (wt%): Cu 14-18, S 22-28, Zn 5-7, Fe 23-28, SiO_2 11-17, H_2O 8-10. The charge is processed by roasting, smelting, converting, refining and casting to produce anode copper. The slag from the reverberatory furnace is fumed to produce zinc oxide dust which is sent to the zinc circuit. The off-gases from the copper roasters, reverberatory furnace and converters are cleaned by Cottrell electrostatic precipitators; the gases from the reverberatory furnace and converters are further processed by passage through a Dracco baghouse. The dusts from the Cottrells are recycled to the reverberatory furnace, while the baghouse dust is sent to the zinc circuit. The bulk of the gases are vented to the atmosphere via a 825 foot high stack.

4. SAMPLES AND ANALYSIS

(I) Samples Studied

Zinc and copper concentrates from individual orebodies and five premixed products were obtained from HBMS in April 1979. The samples of concentrates from the individual orebodies, the two Hudson Bay blends and the one Fox-Ruttan blend were grab samples from the plant. The two remaining blends (Table 1) representing the feed to the copper and the zinc circuits (minus the flux) were prepared in the laboratory at HBMS. The chemical analyses and mineral constituents of the various samples are shown in Tables 2 and 3, respectively. The smelter dusts studied were collected from the Cottrell precipitators of the zinc and copper roasters, and from the Dracco baghouse in the

copper smelter. Baghouse samples No. 1 and 2 are dusts from the same baghouse. The chemical analyses and the identity of these dusts are shown in Tables 4 and 5, respectively.

(II) Analytical Methods

Samples of concentrates were studied using an ore microscope, an electron microprobe equipped with an energy-dispersive analyzer, a scanning electron microscope and an X-ray (Debye-Scherrer) camera in order to identify the minerals and to try to determine directly mercury carriers. Among the minerals observed (Table 3), only tetrahedrite and tennantite were found to contain detectable mercury (300 ppm or more) by electron microprobe.

Since most of the minerals found in the concentrates contained mercury in amounts below the detection limit of the electron microprobe, attempts were made to segregate "pure" samples of the important constituents. The samples were purified by repeated passage through a magnetic separator and/or by separation employing heavy, organic liquids. "Pure" sphalerite, chalcopyrite pyrite and bornite were prepared. Their compositions were determined employing the microprobe (Table 6); their mercury contents were established by wet chemical methods (Table 7).

Pyrrhotite- and silicate-rich fractions were also segregated and analyzed for mercury; however, because of the low proportions of these minerals in the fractions, the observed mercury contents did not represent the pure minerals. "Pure" tetrahedrite or tennantite could not be produced because of

their low concentrations in the samples and the difficulty of their separation from other minerals. The mercury concentrations of these minerals were determined using an electron microprobe; however, the low accuracies of these analyses are due to the low sensitivity of the instrument for mercury.

Chemical analyses for mercury were performed at CANMET using the cold vapour atomic absorption method[5]. Problems were encountered with the analyses of these samples. The reproducibilities of mercury concentration values in zinc concentrates, sphalerite and zinc-rich materials were normally within 10%; reproducibilities in copper concentrates, chalcopyrite, copper-rich fractions, pyrite, pyrrhotite-rich and silicate-rich samples were usually within 30% of each other. Based on the concentration of the major constituents, the samples were homogeneous. Because of this unexpectedly low reproducibility, selected samples were also analyzed by commercial laboratory. The results of CANMET's and those of the commercial laboratory were within ±20% agreement. This possibly suggests that a variable mercury distribution exists in the sulphides. In this report CANMET's analytical data are used for the calculations.

5. RESULTS

I. ZINC AND COPPER CONCENTRATES

Referring to Table 1, it can be seen that zinc concentrate from Fox Lake-Ruttan Lake ores contains 200 ppm Hg; the Hudson Bay concentrate blended from Snow Lake, Chisel Lake and Flin Flon concentrates contains 88 ppm Hg. The Pine Point concentrate contains no detectable mercury. The calculated mercury content of the zinc smelter feed is 115 ppm. The blend prepared by HBMS analyzed 130 ppm Hg. The actual plant feed is cited[6] to contain approximately 110±30 ppm Hg, which is in good agreement with our findings. Of the total feed to the zinc circuit, 30.6% of the mercury input is from Hudson Bay concentrate and 69.4% is from Fox Lake-Ruttan Lake concentrates.

The mercury contents of the copper concentrates are also summarized in Table 1. Hudson Bay, Ruttan Lake and Fox Lake concentrates contain 18 ppm, 28 ppm and 36 ppm Hg, respectively. The calculated mercury content of the smelter feed (without fluxing sand) is 21 ppm. The blend prepared by HBMS analyzed 20 ppm Hg. The actual plant feed contains approximately 30 ppm Hg*[6]. Of the calculated mercury input 62.4% is contributed by the Hudson Bay concentrate, 15.9% by Ruttan Lake and 21.7% by Fox Lake. Whitehorse concentrate contains no detectable mercury.

More detailed chemical analyses of these various samples are given in Table 2.

As can be seen from Table 6, among the minerals observed in the concentrates only sphalerite, chalcopyrite, tetrahedrite

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* Sample taken during different time period.

and tennantite contain significant mercury. The sphalerite contributes 99% of the total mercury in the zinc concentrate and more than 50% in the copper concentrate. The mercury is present in solid solution in sphalerite. Chalcopyrite contributes approximately 20% of the mercury in copper concentrates; however, this is variable. Tetrahedrite, tennantite, pyrite and possibly other minerals contain the remaining 4 to 32% of the mercury in copper concentrates. Detailed discussions of the results follow.

(a) Zinc Concentrate from Fox Lake-Ruttan Lake

The zinc concentrate blend from Fox Lake-Ruttan Lake contains the highest mercury concentration (200 ppm) of all the samples studied. The sphalerite, chalcopyrite and pyrite in this concentrate contain 230 ppm, 13 ppm and 8 ppm Hg, respectively. Since all of the zinc (50.4 wt%) in the concentrate is associated with the sphalerite and all of the copper (1.8 wt%) is in the form of chalcopyrite, the calculated contribution of the sphalerite to the total mercury content is 197 ppm (98.3% of the total) and of the chalcopyrite it is 0.7 ppm (0.4% of the total). The balance of the mercury is associated with pyrite. These data are summarized in Table 7.

(b) Zinc Concentrate from Pine Point

The Pine Point concentrate has the highest zinc concentration (58.3 wt%) and contains no detectable mercury.

(c) Zinc and Copper Concentrates from Flin Flon

The zinc concentrate from the Flin Flon orebody contains 74 ppm Hg. The mercury concentration of the copper concentrate is 14 ppm. In the concentrates, the mercury contents of the sphalerite, chalcopyrite, tetrahedrite-tennantite and pyrite are 95 ppm, 7 ppm, 700 ppm and 4 ppm, respectively. The highest mercury content (5800 ppm) of all the samples was found in the tetrahedrite of the Flin Flon concentrate (Table 6). As shown in Table 7, sphalerite contains 98.6% of the total mercury in the zinc concentrate, and 52.9% of the total mercury in the copper concentrate. Chalcopyrite, tetrahedrite-tennantite and other minerals such as pyrite contribute 23%, 18% and 6%, respectively to the mercury content of the copper concentrate.

(d) Zinc and Copper Concentrates from Chisel Lake

The zinc concentrate from this orebody contains 52.4 wt% Zn, 0.62 wt% Cu and 99 ppm Hg. The copper concentrate contains 7.49 wt% Zn, 18.1 wt% Cu and 22 ppm Hg. The sphalerite, chalcopyrite, tennantite-tetrahedrite, pyrrhotite and pyrite contain 109 ppm, 2ppm, 300 ppm, 1.5 ppm and 1 ppm Hg, respectively. If all the zinc found in the zinc concentrate is in the form of sphalerite, the corresponding mercury contribution of the sphalerite to the total mercury is 99 ppm Hg, which accounts for 99.7%. If the copper in the copper concentrate is in the form of chalcopyrite, the chalcopyrite contributes 1 ppm Hg (5%). The contribution of the sphalerite in the copper concentrate is 14 ppm Hg, indicating that the sphalerite is the major carrier of mercury (62.9%).

Tetrahedrite contributes 22.3% and pyrrhotite plus pyrite contribute 9.8%.

(e) Copper Concentrate from Ruttan Lake

Of the various copper concentrates investigated that from Ruttan Lake contains the second highest concentration of copper (28.5 wt%) and of mercury (28 ppm). In the same concentrate the sphalerite, chalcopyrite and pyrite contain approximately 200 ppm, 17 ppm and 11 ppm Hg, respectively.

The calculated mercury contribution of the sphalerite is 11 ppm (37.2% of the total mercury), of chalcopyrite is 14 ppm (49.3% of the total mercury) and of pyrite, pyrrhotite and possibly also tetrahedrite is approximately 4 ppm (13.5% of the total mercury).

(f) Copper Concentrate from Fox Lake

This concentrate has the highest mercury content (36 ppm) of all concentrates fed to the copper smelter. The sphalerite, chalcopyrite and pyrite contain 300 ppm, 8 ppm and 3 ppm Hg, respectively. Some mercury is probably contained in the tennantite however, its concentration is too low to be able to detect mercury. The calculated mercury contribution of sphalerite to the total mercury content is 29 ppm (79.1%), of chalcopyrite 6 ppm (17.0%). The remaining 1 ppm (3.9%) is contained in other minerals.

(g) Copper Concentrate from Snow Lake

The copper concentrate from the Snow Lake orebody contains 18 ppm Hg. The sphalerite, chalcopyrite, tetrahedrite,

pyrite and pyrrhotite in this concentrate contain 240 ppm, 8 ppm, 800 ppm, 7 ppm and 1 ppm Hg, respectively. The calculated mercury contribution of the sphalerite to the total mercury in the concentrate is 11 ppm (62% of the total), of the chalcopyrite it is 5 ppm (25% of the total), of the tetrahedrite it is 2 ppm (12% of the total). The other minerals such as pyrite and pyrrhotite account for the remainder.

(h) Copper Concentrate from Whitehorse

The copper concentrate from the Whitehorse orebody contains the lowest concentration of mercury (<1 ppm) and the highest copper (46.1 wt%) of all copper concentrates fed to the copper extraction circuit. As shown in Table 3, the mineralogy of this concentrate differs from the others. Only bornite in the concentrate contains a detectable amount of mercury (~4 ppm).

II. SMELTER DUSTS

With the current operational practice at HBMS' Flin Flon plant (Fig. 1), essentially all the mercury in the concentrates is volatilized as the concentrate is roasted. Any remaining mercury is evolved in the reverberatory furnace (T~1200°C). This is verified by the fact that the mercury concentration of the zinc roaster calcine is <1 ppm[6], while the average feed to the roaster contain 115 ppm Hg. Similarily, the copper roaster calcine contains <1 ppm Hg[6] as compared to the feed having 21 ppm Hg. Furthermore, the reverberatory furnace copper matte contains <<1 ppm Hg. Balloon flue dusts

are also expected to have a low mercury content since the flue temperatures are relatively high. These dusts are recycled to the reverberatory furnace. Each of the dusts in the zinc and copper processing circuits, that contain significant concentrations of mercury, will be discussed in detail below.

The chemical compositions of the important smelter dusts from the HBMS Flin Flon operations are listed in Table 4 and the constituent compounds are given in Table 5. Since these dusts were carried by off-gases from roasters, the reverberatory furnace or converters, the bulk of the particles are small, usually <1 μm for the baghouse dust, 40 to 200 μm for the zinc circuit electrostatic precipitator dust and <5 μm to 70 μm for the copper circuit electrostatic precipitator dust. The differences in size of the dusts possibly relates to the origin of the dust; i.e., the coarser being the "original" size of the feed/product and the finer being a "fused" material. The texture of the particles is complex as is their constitution.

(a) Zinc Electrostatic Precipitator Dust

The electrostatic precipitator dust in the zinc circuit contain 11 ppm Hg. As compared to other dusts in the smelter, the particles sizes of this dust are relatively coarse, being primarily between 40 and 200 μm, with some as large as 450 μm.

Due to the roasting process, most particles have a spongelike texture (Figure 2) and consist primarily of zinc ferrite, Fe_2O_3, and minor amounts of Fe_3O_4, ZnO and (Zn,Fe)S. Some partially calcined particles have sphalerite cores surrounded

by zinc ferrite, Fe_2O_3, zinc sulphate(?) and an outermost rim of ZnO. A few metallic zinc-copper or zinc spherules with ZnO or ZnS rims have apparently solidified from liquid droplets (Fig. 3). Minor quantities of chalcopyrite, pyrite, pyrrhotite, quartz and silicate minerals are also present. Slightly more than 1 wt% of the dust is composed of white spherical aggregates (approximately 30 to 100 μm in diameter) of fine-grained ZnO, and minor hydrous(?) Zn, Fe, Pb sulphates/arsenates (Fig. 3, 4). Some of the hydrolysis could have occurred during the storage of samples. The aggregates were subsequently separated from the dust in a non-magnetic fraction by the use of a magnetic separator. It was found that these aggregates contained approximately 115 ppm Hg and that their partial chemical compositions (Zn, Pb, Fe, $SO_3^=$, As), IR spectra and X-ray powder diffraction patterns are comparable to those of copper baghouse dust. The mercury carried by these aggregates is approximately 10% of the mercury in the precipitator dust. Assuming that the unoxidized sphalerite core in the partially calcined particles retains its mercury and that its average mercury content is 145 ppm, the unoxidized sphalerite contains 49% of the total mercury in this dust. The carriers for the remaining 40% of the mercury in the Cottrell dust still remain unknown.

(b) Copper Electrostatic Precipitator Dust

Of all the smelter dusts studied, electrostatic precipitator dusts from the copper circuit have the most complicated textures and the most complex particle constituents. Approximately

one-third of the dust is fine-grained (<15 μm in size) spherules or hollow spherical grains (Fig. 5, 6); these have apparently condensed from the vapor phase or have solidified from a liquid phase. Approximately one-fifth of the dust particles are fine, irregularly shaped, spongelike, calcined aggregates. The majority of the spherules, the hollow spherical grains and the spongelike aggregates are Cu-Fe-Zn oxides, Cu sulphides, Fe and Zn oxides, silicates of Fe, Pb, Cu and Zn, silicates of Mg, Fe and Al and elemental sulphur or other low atomic number sulphur compounds. The balance of the dust is comprised of angular mineral grains, primarily chalcopyrite, pyrite, bornite, copper sulphides, quartz and silicate minerals. The mineral grains have sizes varying from less than 5 μm to 70 μm. Because the temperature of the roasting operation, some of the chalcopyrite and bornite particles show partial decomposition to other Cu-Fe sulphides.

Copper precipitator dust contains 366 ppm of mercury. Despite the high mercury content, only one mercury-bearing grain was found by electron microprobe. The following elements were detected in the grain (wt%): Hg 1.4-3.3, Pb 0.1-0.4, As 0.2-1.4, Al 0.1-1.6, Se 0.2-1.3, S 4.6-9.5, Fe 0.2-0.6, Cu 0.6-1.1, Zn 0.2-0.9 and Cl 0.2-0.4. Because elements with atomic numbers less than 11 could not be detected by the electron microprobe, the total composition of the grain could not be established.

(c) Dracco Copper Baghouse Dust

Two baghouse samples, No. 1 and No. 2, were studied. Their particle constituents (Table 5) and chemical compositions (Table 4) are similar; however, their mercury contents differ significantly being 318 ppm Hg and 223 ppm Hg for samples No. 1 and No. 2, respectively.

The major constituent of the baghouse dust is an extremely fine-grained (<1 μm) zinc oxide (Fig. 7, 8) which may have condensed/sublimed from furnace off-gas. A major portion of the dust is unidentified hydrous(?) Zn, Pb, Fe and Cu sulphates/arsenates, and trace amounts of coarse-grained (1-20 μm) spherules of silicates, sulphides and metals (Table 5) also occur in the dust. These larger particles could have resulted from liquid droplet carryover. The sizes of most of the particles in the baghouse dust are extremely fine. It was impossible to resolve individual particles even with a scanning electron microscope. This observation is consistent with a vapour formation mechanism. Identification of these particles was based on data from X-ray powder diffraction patterns, on infrared spectroscopy and on wet chemical analyses to identify $SO_4^=$, OH^- and H_2O. Some of the coarse-grained spherules were analyzed by electron microprobe. Despite the difficulty encountered in characterizing these particles, most of the major and minor phases were identified. Preliminary results indicate that the mercury in the dust is associated with a fine-grained mixture of zinc oxide and unidentified hydrous(?) sulphates/arsenates. At this time, it is not possible to state whether the Hg is

present as a separate, trace phase, as a solid solution in ZnO, etc., or as an adsorbed layer on the surface of all particles.

6. DISCUSSION AND CONCLUSIONS

Mercury in concentrates processed by HBMS at Flin Flon is in solid solution in sphalerite, chalcopyrite and tetrahedrite or tennantite. In the zinc concentrates, sphalerite accounts for more than 98% of the mercury input. In the copper concentrates sphalerite contains approximately 50% of the mercury and chalcopyrite and tetrahedrite-tennantite are each approximately equal carriers of mercury. Since the mercury is in solid solution in the sphalerite, it cannot be separated from the zinc concentrate by employing minerals beneficiation techniques. Some lowering (~20%) of the mercury burden to the copper smelter could be achieved if the tetrahedrite-tennantite could be rejected. However, this could require a sub-circuit to recover some of the Ag and Cu, and to collect the As and Sb. The most significant (~50%) reduction in the amount of mercury entering the copper circuit could be accomplished by improving the copper-zinc sulphide separation in the milling process. This separated zinc sulphide would be sent to the zinc roasters, and this would not result in a net reduction of the mercury input in the smelter as a whole.

As was pointed out earlier, under current pyrometallurgical operating conditions at HBMS, essentially all the mercury in the concentrates is volatilized when the concentrate is roasted. Any small amount of mercury remaining will be evolved in the reverberatory furnace. Table 8 lists the approximate evolution

temperatures of mercury from various minerals and compounds. There could be some variation in the temperatures, due possibly to a different formation/metamorphosis temperature of the minerals.

As the furnace off-gases enter the gas cleaning circuit, they cool and the mercury can recombine with particulates or can co-precipitate with other gaseous components. Mercury concentrations in smelter dusts are expected to vary with the matrix (i.e., grain size, composition, amount), possibly with the gaseous components, and especially with the temperature of the dust collector; the lower the temperature, the higher the mercury content of the dusts.

Dust collected at ≈180°C from the copper roasters ESP contains fine-grained copper sulphides and has the highest mercury content of all smelter dusts studied. Electrostatic precipitator dust from the zinc circuit, collected at ≈275°C, contains mainly coarse-grained Fe_2O_3, $ZnFe_2O_4$ and ZnO and has the lowest mercury content. Baghouse dust from the copper circuit, containing what appears to be primarily sublimed ZnO, has an intermediate mercury concentration.

The path of mercury in the copper and zinc circuits is shown in Fig. 9, and the mercury balance in the smelter is given in Table 9. Approximately 69% of the mercury total entering the smelter is contained in the zinc concentrate, while 31% is in the copper concentrate. Only 2% of the mercury total is recycled with the dust from zinc electrostatic precipitators. About 85% of the mercury entering the stack is from the zinc circuit, while only 15% is from the copper circuit. This is

attributed primarily to the relatively high temperatures of the zinc Cottrell precipitators. In the copper circuit, 22% of the mercury total is contained in the roasters dust, which is recycled to the reverberatory furnace. The copper baghouse dust contains 11% of the total mercury, and this is fed to the zinc smelter.

It is apparent that if copper circuit dusts were separately processed before they rejoin the main stream, up to 33% of the mercury total could be isolated. If the temperature of the off-gas from the zinc roasters could be lowered, then significantly more mercury would collect in the dusts. The dusts would have to be processed to remove mercury before recycling to the zinc circuit. To keep stack gases above the dew point of acid mist and to maintain adequate draft on the stack, additional burners may be required to reheat the off-gases thereby increasing energy requirements for the process.

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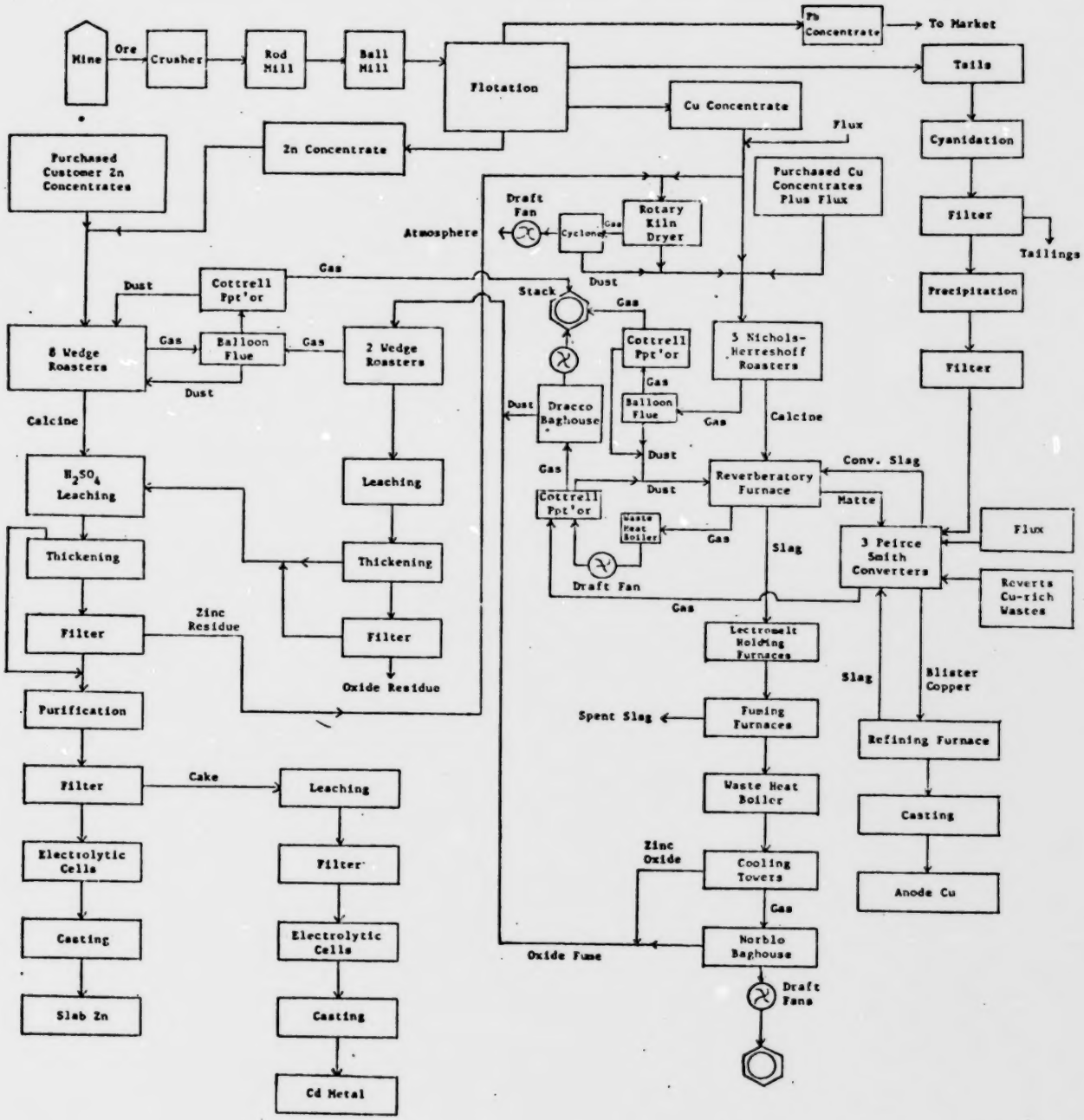

Fig. 1 - Flow sheet of copper and zinc processing circuits for Hudson Bay Mining and Smelting Company, Limited, Flin Flon, Manitoba (2,3,4).

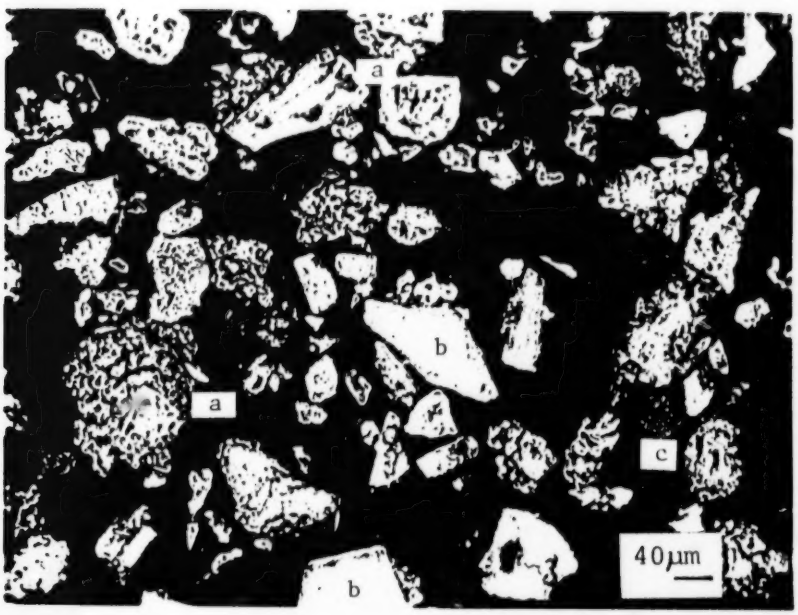

Fig. 2 - SEM backscattered electron image of polished section of zinc ESP dust, showing calcination textures. The spongelike grains (a) consist mainly of Fe_2O_3, $ZnFe_2O_4$, minor Fe_3O_4, ZnO and (Zn, Fe) sulphate; some incompletely calcined grains (b) have relic (unreacted) sphalerite cores with $ZnFe_2O_4$, (Zn, Fe) sulphate and ZnO rims. Most of the small spherules (c) consist of fine-grained aggregates of ZnO and hydrous (?) Zn, Fe, Pb sulphate/arsenate.

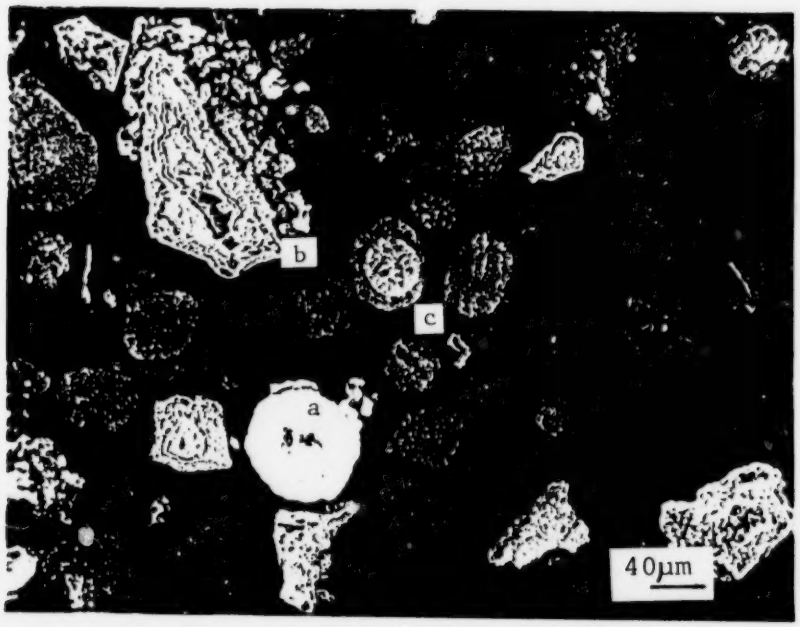

Fig. 3 - SEM backscattered electron image of polished section of the non-magnetic fraction (0.7 ampere current to magnet) of the zinc precipitator dust. ZnS spherules with a metallic (Zn, Cu) core (a) are shown. The calcined grains (b) consist mostly of $ZnFe_2O_4$, Fe_2O_3 and minor amounts of Fe_3O_4 and ZnO. The spherical aggregates (c) consist mainly of extremely fine-grained ZnO and hydrous(?) Pb, Zn, Fe, sulphate/arsenate.

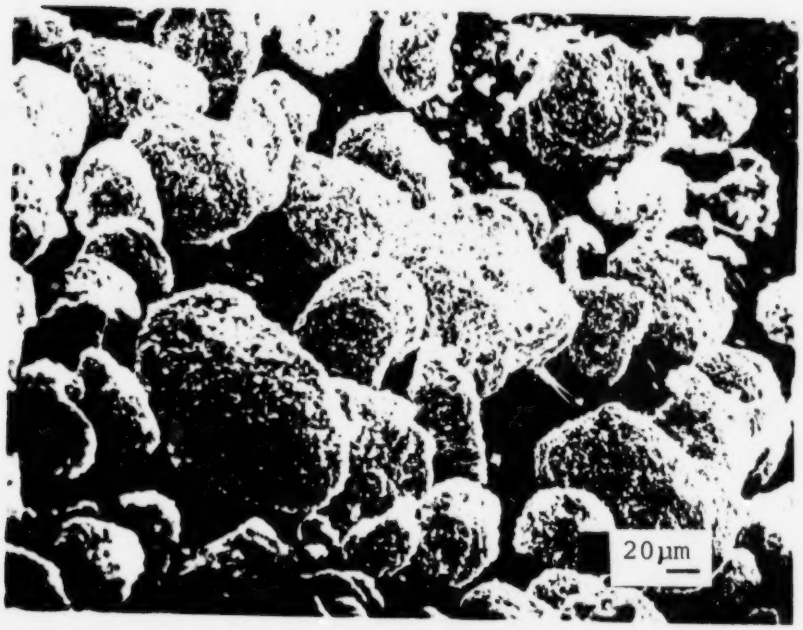

Fig. 4 - SEM photograph of the non-magnetic fraction (1.4 ampere current to magnet) of the zinc precipitator dust. White spherical aggregates of ZnO and hydrous (?) Zn, Fe, Pb sulphate/arsenate can be seen.

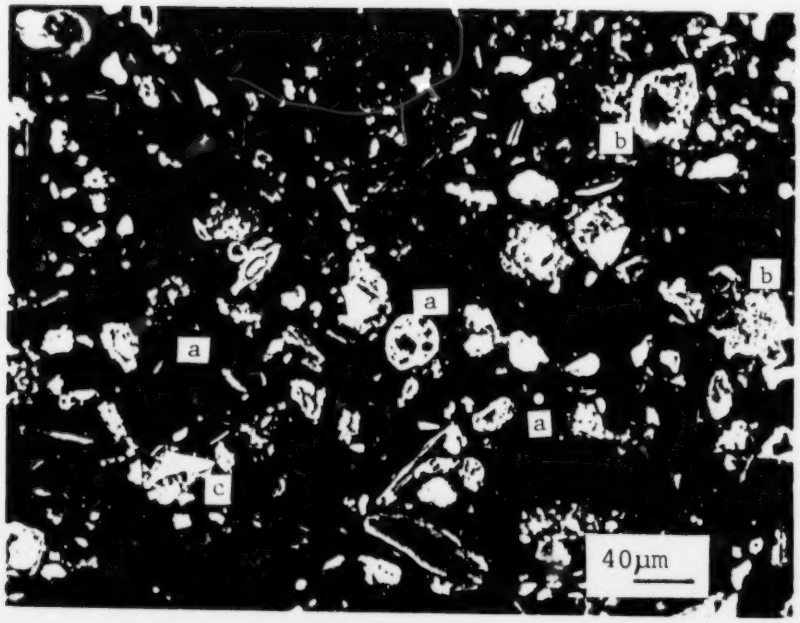

Fig. 5 - SEM backscattered electron image of polished section of copper precipitator dust, showing solid and hollow spherical grains (a)of (Fe, Cu, Zn) oxides, (Al, Fe, Mg) silicates, (Cu, Fe, Zn, Pb) silicates and sulphides, and volatile sulphur compounds. The spongelike or irregularly shaped grains (b) are primarily Cu sulphides, (Cu, Fe) oxide, (Cu, Fe) sulphate and (Fe, Zn) oxide. The angularly shaped grains (c) are mainly chalcopyrite, bornite, covellite, pyrite, quartz and silicate minerals.

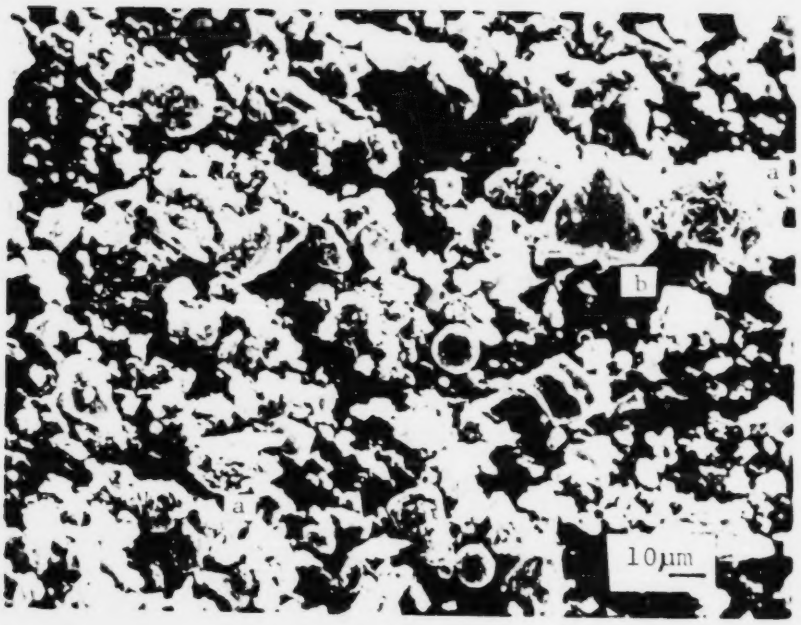

Fig. 6 - SEM photograph of copper precipitator dust, showing spherical and calcined grains (a) of (Cu,Fe,Zn) oxide, Cu sulphides, Fe, Pb, Cu and Zn silicates, and angular-shaped grains (b) of chalcopyrite, pyrite, bornite, quartz and silicate minerals.

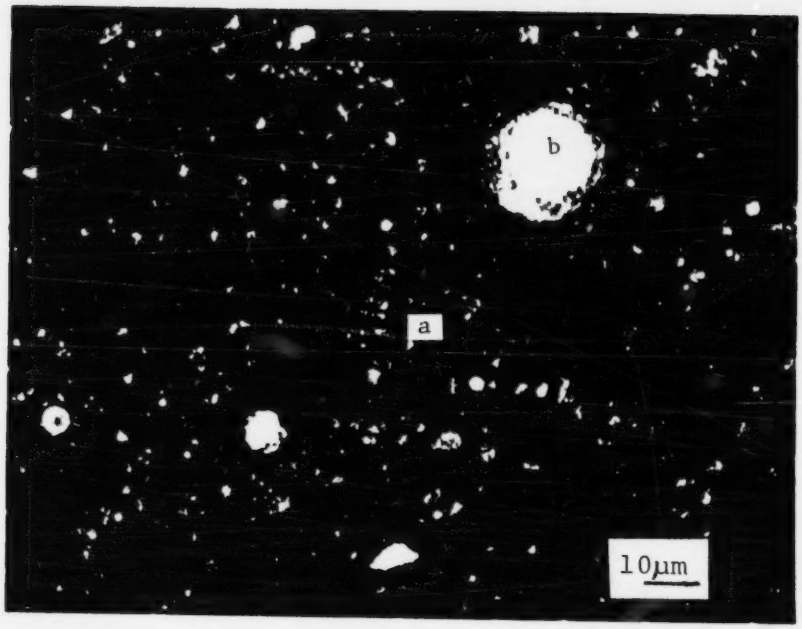

Fig. 7 - SEM backscattered electron image of polished section of Dracco baghouse dust (No. 1), showing extremely fine-grained (a) ZnO and hydrous(?) Zn, Pb, Fe, Cu sulphate/arsenate matrix, and coarse-grained spherules (b) of metallic copper with Cu_2S rims.

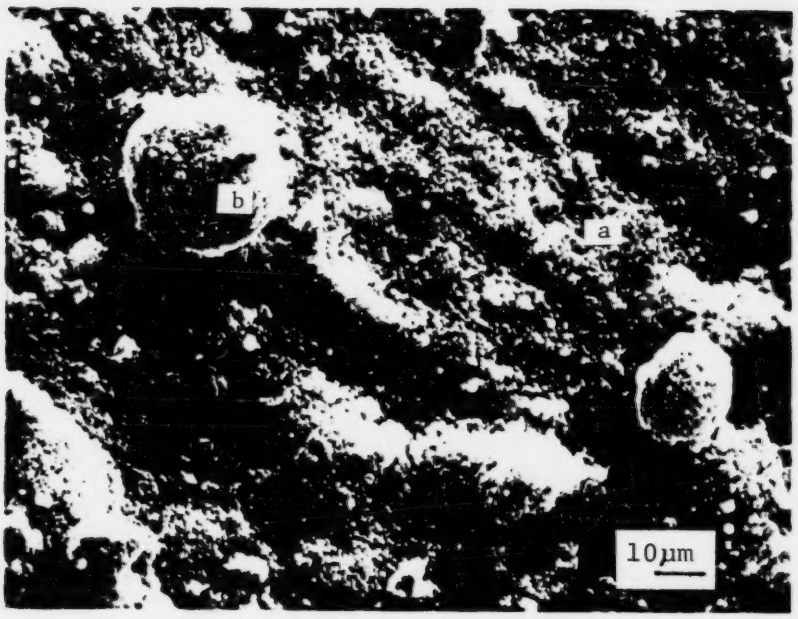

Fig. 8 - SEM photograph of Dracco baghouse dust (No. 2), showing extremely fine-grained ZnO and hydrous (?) Zn, Pb, Fe, Cu sulphate/arsenate (a). The coarse-grained spherules (b) are mostly of metallic Cu, Cu_2S, (Zn, Fe, Cu) silicates, Zn, Al, Fe, Pb silicates (Zn, Fe, Cu) sulphide and (Fe, Cu, Zn) oxide.

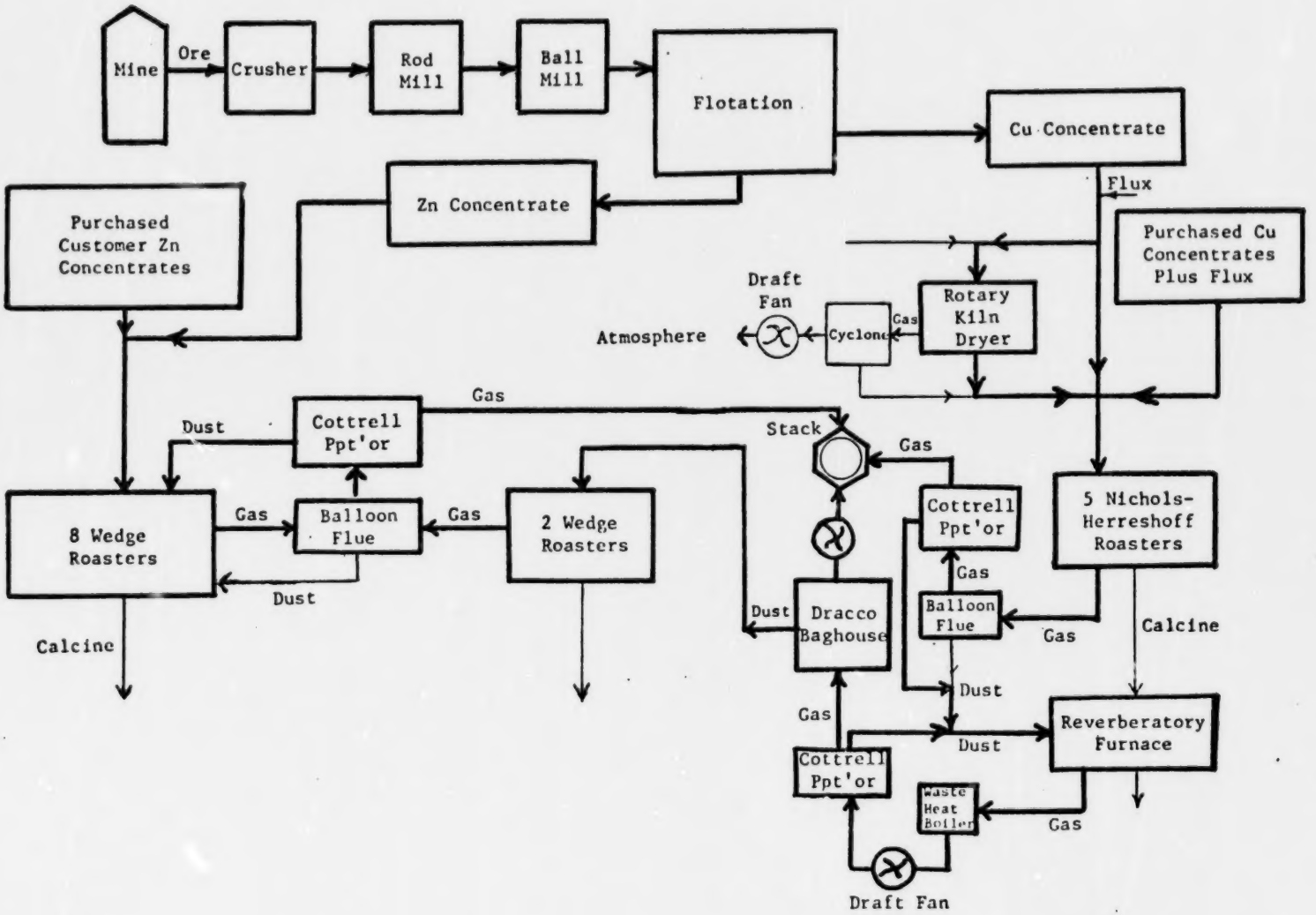

Fig. 9 - Partial flow sheet of zinc and copper processing circuits at HBMS. Bold lines indicate main mercury streams.

Table 1 - Distribution of mercury in mill concentrates from Hudson Bay Mining and Smelting Co., Limited.

	Source of mill conc.	Proportion of conc. in smelter feed	Analyzed Hg content of conc.	Hg contribution to smelter feed	Composition of blended conc.
Zinc smelter feed: 115 ppm Hg (calc.)	"Hudson Bay"	40%	88 ppm	30.6%	60% Chisel Lake (99 ppm Hg) 40% Snow Lake and Flin Flon (74 ppm Hg)
	Fox-Ruttan L.	40%	200 ppm	69.4%	
	Pine Point	20%	<1 ppm	0	
Copper Smelter feed: 21 ppm Hg (calc.)	"Hudson Bay"	70.8%	18 ppm	62.4	60% Snow Lake (18.4 ppm Hg) 36% Flin Flon (13.8 ppm Hg) 4% Chisel Lake (22.4 ppm Hg)
	Ruttan Lake	11.5%	28.2 ppm	15.9%	
	Fox Lake	12.2%	36.4 ppm	21.7%	
	Whitehorse	5.5%	<1 ppm	0	

Table 2(a) - Chemical analysis of Zinc concentrates from Hudson Bay Mining and Smelting Co., Limited

Element	Chisel Lake	Flin Flon	Hudson Bay**	Fox-Ruttan Lake	Pine Point
(wt%)					
Cu	0.62	0.90	0.77	1.78	0.02
Zn	52.40	46.03	50.46	50.40	58.26
Pb	1.00*	0.69	0.58	0.14	1.20
Fe	11.31	13.48	11.01	11.88	2.73
S	30.6*	32.75	32.80	33.24	32.77
Si	4.58*	3.40	0.81	0.48	0.10
(ppm)					
Hg	99	74	88	200	<1
As	1500*	4600	3950	<250	<250
Sb	150*	-	<100	<100	<100
Bi	-	-	20	<20	<20
Cd	1300	1300	1366	1500	1191
Ag	41.7*	-	50	23	4
Au	1.4*	-	1.1	0.7	0.2
Total	100.8	97.9	97.0	98.1	95.3

* Analyses performed on other similar samples by Hudson Bay Mining and Smelting Co., Ltd.

**Blend sample consisting of 60% Chisel Lake concentrate and 40% Snow Lake and Flin Flon concentrates.

Table 2(b) - Chemical analysis of Copper concentrates from Hudson Bay Mining and Smelting Co., Limited

Element (wt%)	Chisel Lake	Flin Flon	Snow Lake	Hudson Bay***	Fox Lake	Ruttan Lake	Whitehorse
Cu	18.10	16.23	20.63	20.55	25.76	28.51	46.08
Zn	7.49	4.57	2.77	4.23	5.52	3.14	0.50
Pb	1.07*	0.48*	0.10*	0.36	0.28	2.07	0.03
Fe	23.88	24.35	31.07	28.41	27.87	27.64	10.30
S	30.0*	30.00*	30.0*	31.65	33.91	33.50	18.76
Si	4.58*	4.67*	2.43*	3.92	2.08	1.31	5.78
(ppm)							
Hg	22.4	13.8	18.4	18	36.4	28.2	<1
As	-	-	-	5060	487	<250	<250
Sb	1780*	760*	670*	610	<100	<100	<100
Bi	-	-	-	35	<20	348	1304
Cd	200	100	100	100	186	151	<100
Ag	696*	224.2*	27.5*	175	177	223	∿300
Au	47.5*	10.8*	4.2*	4.9	3.3	4.6	26.0
Total	∿85.4	∿80.4	∿87.1	∿89.7	∿95.5	∿96.3	∿81.7

* Analyses performed on other similar samples by Hudson Bay Mining and Smelting Co., Ltd.

***Blend sample consisting of 60% Snow Lake concentrate, 36% Flin Flon concentrate and 4% Chisel Lake concentrate.

Table 3(a) - Minerals observed in mill concentrates from Hudson Bay Mining and Smelting Co., Ltd.

Zinc Concentrates
1. Chisel Lake, Manitoba Sphalerite, chalcopyrite, pyrite, quartz, calcite, dolomite, pyrrhotite, silicates; trace amounts of galena, miargyrite, arsenopyrite, tennantite, stannite, rutile and ilmenite-pyrophanite
2. Pine Point, N.W.T. Sphalerite, silicates, quartz, calcite, pyrite; trace galena, arsenopyrite, magnetite
3. Flin Flon, Manitoba Sphalerite (containing numerous inclusions of chalcopyrite), pyrite, silicates, quartz, pyrrhotite, chalcopyrite, arsenopyrite, galena; trace hematite, tetrahedrite, bornite, chalcocite
4. Fox-Ruttan Lake, Manitoba Sphalerite (containing numerous exsolved blebs of chalcopyrite), pyrite, chalcopyrite, silicates, pyrrhotite; trace galena

Table 3(b) - Minerals observed in mill concentrates from Hudson Bay Mining and Smelting Co., Ltd.

Copper Concentrates
1. Fox Lake, Manitoba Chalcopyrite, sphalerite (containing exsolved blebs of chalcopyrite), pyrite, pyrrhotite, silicates, hematite, quartz; trace tennantite, bornite, covellite, molybdenite
2. Ruttan Lake, Manitoba Chalcopyrite, sphalerite, pyrite, pyrrhotite, quartz, silicates; trace galena, native bismuth, molybdenite
3. Chisel Lake, Manitoba Chalcopyrite, silicates (biotite, etc.), quartz, pyrite, sphalerite, magnetite; trace pyrrhotite, tennantite-tetrahedrite galena, bournonite, pyrargyrite, electrum
4. Snow Lake, Manitoba Chalcopyrite, pyrite, sphalerite, pyrrhotite, biotite, quartz and other silicates; trace tetrahedrite, galena arsenopyrite, tennantite, magnetite
5. Flin Flon, Manitoba Chalcopyrite, pyrite, silicates, sphalerite, pyrrhotite; trace tetrahedrite-tennantite, arsenopyrite, magnetite
6. Whitehorse, Yukon Bornite, silicates, quartz, chalcopyrite, chalcocite, digenite; trace sphalerite, pyrite, tetrahedrite, galena, molybdenite, covellite

Table 3 - Footnote
Nominal composition of minerals cited

Arsenopyrite	FeAsS	Biotite	$K(Mg,Fe)_3(Al,Fe)\cdot Si_3O_{10}(OH,F)_2$
Bornite	Cu_5FeS_4	Bournonite	$PbCuSbS_3$
Calcite	$CaCO_3$	Chalcocite	Cu_2S
Chalcopyrite	$CuFeS_2$	Covellite	CuS
Digenite	Cu_9S_5	Dolomite	$CaMg(CO_3)_2$
Electrum	(Au,Ag)	Galena	PbS
Hematite	Fe_2O_3	Ilmenite	$FeTiO_3$
Magnetite	Fe_3O_4	Miargyrite	$AgSbS_2$
Molybdenite	MoS_2	Pyrargyrite	Ag_3SbS_3
Pyrite	FeS_2	Pyrophanite	$MnTiO_3$
Pyrrhotite	$Fe_{1-x}S$	Quartz	SiO_2
Rutile	TiO_2	Sphalerite	(Zn,Fe)S
Stannite	Cu_2FeSnS_4	Tennantite	$(Cu,Fe)_{12}As_4S_{13}$
Tetrahedrite	$(Cu,Fe)_{12}Sb_4S_{13}$		

Table 4 - Chemical analysis of smelter dusts from Hudson Bay Mining and Smelting Co., Limited

Element	Electrostatic Precipitator Zn Cottrell	Cu Cottrell	Dracco Baghouse No. 1	No. 2
(wt%)				
Zn	53.01	6.87	31.14	33.78
Pb	0.33	0.06	10.88	9.67
Fe	11.18	22.33	2.41	2.17
Cu	1.40	17.10	3.54	3.38
S_{total}	4.69	12.48*	9.90	9.34
$S_{SO_4}^{=}$	3.45	4.34	9.46	9.31
As	0.12	0.50	3.06	3.31
Cd	0.01	0.03	1.75	1.87
Hg (ppm)	11	366	318	223
TOTAL	71	60	63	64

*Including elemental S 0.52%

Table 5 - Phases observed in the smelter dusts from Hudson Bay Mining and Smelting Co., Limited

1. Zinc precipitator dust
   ZnO, ferrite ($ZnFe_2O_4$, composition variable), sphalerite, Fe_2O_3, Fe_3O_4. Minor to trace amounts of chalcocite, pyrrhotite, chalcopyrite, pyrite, quartz, zinc metal, (Zn,Cu) alloy, (Zn,Fe,Al,Cu) silicate, (Zn,Fe) silicate, (Zn,Fe,Pb) silicate, (Zn,Fe) sulphate, hyrdous(?) (Zn, Fe,Pb) sulphate/arsenate.

2. Copper precipitator dust
   (Cu,Fe) oxide, (Cu,Fe,Zn) oxide and sulfate(?), Fe_2O_3, $ZnFe_2O_4$, covellite, chalcocite, chalcopyrite, bornite and other Cu sulfides and (Cu,Fe) sulfides, silicates of Fe, Zn, Pb and Cu, and/or Mg and Al, elemental sulphur and other volatile sulphur compounds, pyrite and quartz. Minor amounts of mineral grains of (Al,Fe,K) silicates, (Mg,Fe,Cu) silicate and (Mg,Fe) silicate. Trace amounts of sphalerite, tetrahedrite and a (Hg,Cu,Zn,Si,S,As,O, etc.) compound.

3. Dracco baghouse dust (No. 1 and No. 2)
   More than 97% are less than 1 μm sized grains of ZnO, and possibly also hydrous(?) (Zn,Pb,Fe,Cu) sulphates/ arsenates. Approximately 2-3% are 1-20 μm sized spherules of Cu metal (frequently with a Cu_2S rim), Cu_2S, (Zn,Fe,Cu) silicate, Fe silicate, (Zn,Al,K,Fe,Pb) silicate, (Fe,Zn,Cu,Ca) silicate, $ZnFe_2O_4$, (Al,K,Fe,Cu,Zn) silicate, (Fe,Zn,Pb,Cu) oxide, (Cu,Fe,Zn) sulphide and (Fe,Cu) oxide, and some angular grains of quartz, chalcopyrite, (Fe,Zn,Cu) silicate, bornite, sphalerite, galena, (Zn,Al,Ca) silicate, (Ca,Al) silicate and (Ca,Fe,Zn,Mg) silicate.

Table 6(a) - Average compositions of sphalerite, chalcopyrite, tetrahedrite-tennantite and other copper sulphide minerals by electron microprobe analysis.

	Chisel Lake				Flin Flon				Snow Lake			
	1. sp	2. cp	3. td	4. td*	5. sp	6. cp	7. td	8. td*	9. sp	10. cp	11. td	12. td*
Zn	57.84	-	3.0	3.2	60.04	-	4.7	5.0	58.46	-	4.7	5.6
Fe	8.16	30.79	4.4	4.3	6.85	31.00	3.1	2.7	7.01	30.47	2.9	2.3
Cu	-	34.85	38.5	43.9	-	34.86	40.5	37.9	-	34.85	39.8	38.4
Ag	-	-	2.4	0.5	-	-	0.8	0.4	-	-	0.1	n.d.
Mn	0.33	-	-	-	0.12	-	-	-	0.87	-	-	-
Hg	n.d.	n.d.	0.03	0.10	n.d.	n.d.	0.07	0.58	0.02	n.d.	0.08	0.26
Sb	-	-	10.7	0.1	-	-	21.1	26.6	-	-	23.7	28.5
As	-	-	14.6	19.5	-	-	5.3	1.4	-	-	3.4	0.7
S	33.44	35.11	27.4	27.9	33.22	35.27	26.0	25.4	33.57	35.21	26.1	25.4
Total	99.77	100.75	101.03	99.5	100.23	101.13	101.6	100.0	99.93	100.53	100.8	101.2

sp = sphalerite, cp = chalcopyrite, td = tetrahedrite-tennantite
bn = bornite, cc = chalcocite, di = digenite,
cv = covellite, nd = not detected

*High-mercury analysis;

Table 6(b) - Average compositions of sphalerite, chalcopyrite, tetrahedrite-tennantite and other copper sulphide minerals by electron microprobe analysis

	Fox Lake			Ruttan Lake		Fox-Ruttan	Pine Point	Whitehorse			
	13. sp†	14. cp	15. td	16. sp†	17. cp	18. sp†	19. sp	20. bn	21. cc	22. di	23. cv
Zn	57.49	-	2.5	60.01	-	58.96	65.25	-	-	-	-
Fe	8.06	30.97	5.4	6.50	31.35	7.45	1.76	11.2	-	-	-
Cu	-	34.38	42.3	-	34.69	-	-	63.6	79.2	77.9	70.0
Ag	-	-	0.3	-	-	-	-	-	-	-	-
Mn	0.22	-	-	0.16	-	0.14	n.d.	-	-	-	-
Hg	0.03	n.d.	n.d.	n.d.	n.d	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Sb	-	-	1.6	-	-	-	-	-	-	-	-
As	-	-	18.5	-	-	-	-	-	-	-	-
S	33.20	34.64	28.5	33.45	34.85	33.40	32.73	25.7	20.4	22.1	29.9
Total	99.00	99.99	99.1	100.12	100.89	99.95	99.74	100.5	99.6	100.0	99.9

sp = sphalerite, cp = chalcopyrite, td = tetrahedrite-tennantite
bn = bornite, cc = chalcocite, di = digenite,
cv = covellite, nd = not detected

†Containing 0.13 wt% Cd

Table 7 - Analyzed chemical composition of purified sphalerite and chalcopyrite, and calculated Hg content and distribution in minerals.

Source	Conc.	Sphalerite		Chalcopyrite		Concentrate			Calc. Hg contrib. in ppm (or in % of tot. Hg)			
		Zn wt%	Hg ppm	Cu wt%	Hg ppm	Zn wt%	Cu wt%	Hg ppm	sph	cp	td	py & po
Chisel Lake	Zn	57.84	109	34.85	2.2	52.40	0.62	99	98.7 (99.7)	0.04	<1 (0.3)**	
	Cu					7.49	18.10	22.4	14.1 (62.9)	1.1 (5)	5.0 (22.3)	2.2 (9.8)
Flin Flon	Zn	60.04	95.2	34.47	6.7	46.03	0.90	74	73.0 (98.6)	0.2 (0.3)	0.8 (1.1)**	
	Cu					4.57	16.23	13.8	7.3 (52.9)	3.2 (23.2)	2.5 (18.1)	0.8 (5.8)
Pine Point	Zn	65.25	<1	-	-	58.26	-	<1	<1	-	-	- -
Fox-Ruttan L.	Zn	58.96	230	34.50	∿13.0	50.40	1.78	200	196.6 (98.3)	0.7 (0.4)	-	2.7 (1.3)
Ruttan Lake	Cu	60.01	200	34.69	16.9	3.14	28.5	28.2	10.5 (37.2)	13.9 (49.3)	-	3.8 (13.5)***
Fox Lake	Cu	57.49	300	34.38	8.3	5.52	25.76	36.4	28.8 (79.1)	6.2 (17.0)	1.4 (3.9)**	-
Snow Lake	Cu	58.46	∿240	34.85	∿7.8	2.77	20.63	18.4	11.4 (62)	4.6 (25.0)	2.2 (12.0)	0.2 (1.0)
Whitehorse	Cu	-	-	63.6*	4.4*	0.50	46.08**	<1	-	-	-	-

*Bornite. **Tetrahedrite-tennantite and pyrite, and pyrrhotite in Chisel Lake.
***Pyrite and other minerals.

Table 8 - Mercury evolution temperatures of various minerals and compounds

Compound or Mineral	Nominal Composition	Approx. Hg Evolution Temperature (°C)	Comments	Reference
Argentite	Ag_2S	280	b	10
Beudantite	$PbFe_3(AsO_4)(SO_4)(OH)_6$	510	a	9
Cerussite	$PbCO_3$	270	a	9
Chalcocite	Cu_2S	500	a	9
Cinnabar	HgS	300	a, c, e,	9, 7, 11
Covellite	CuS	300	a	9
Dyscrasite	Ag_3Sb	840, 900	b	10
Native Mercury	Hg	80	d, e	8, 11
Iron (III) oxide	Fe_2O_3	420	e	11
Freibergite	$(Ag,Cu,Fe)_{12}(Sb,As)_4S_{13}$	320, 420, 470	b	10
Galena	PbS	810	b	10
Goethite	FeO(OH)	270 - 370	a	9
Mercury (II) chloride	$HgCl_2$	80-250; 220	d, e	8, 11
Mercury (I) chloride	Hg_2Cl_2	80-250; 150	d, e	8, 11
Mercury (II) oxide	HgO	270-535; 520	d, e	8, 11
Mercury (II) sulphate	$HgSO_4$	350, 420, 510	e	11
Plumbojarosite	$PbFe_6(SO_4)_4(OH)_{12}$	450	a	9
Proustite	Ag_3AsS_3	470	b	10

Table 8 (cont'd) - Mercury evolution temperatures of various minerals and compounds

Compound or Mineral	Nominal Composition	Approx. Hg Evolution Temperature (°C)	Comments	Reference
Pyrargyrite	Ag_3SbS_3	370	b	10
Pyrite	FeS_2	500 - 520	a, e	9, 11
Sphalerite	(Zn,Fe)S	730 - 750; 600	a, b; e	9, 10, 11
Stephanite	Ag_5SbS_4	340	b	10
Mercury absorbed on the surface of silicate minerals		230	a	9
Tetrahedrite/tennantite	$(Cu,Fe)_{12}(Sb,As)_4S_{13}$	490	a	9

Measurement of mercury evolution during programmed heating at

a - 12°C/min
b - 14°C/min
e - 17.9°C/min

Measurement of mercury evolution during

c - differential heating
d - differential heating for 30 seconds at each temperature setting

Table 9 - Mercury balance for the smelting operations of HBMS

	Circuit	Approx. Hg Concentration (ppm)	Hg Distribution (% of each circuit)	Hg Distribution (% of total circuit)
	Copper Circuit			
Input	- Copper concentrates	21	100	31
Output	- Bag house dust (to zinc circuit)	270	35	11
	- Main stack[6]	-	39	12*
	- Unaccounted	-	26	8*
Recycle	- Roaster dust	355	70	22
	Zinc Circuit			
Input	- Zinc concentrates	115	86	69
	- Baghouse dust (from copper circuit)	270	14	11
Output	- Main stack[6]	-	81	65*
	- Unaccounted	-	19	15*
Recycle	- Roaster dust	10	2	2

*Sum of indicated outputs from total circuit = 100